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Alumina-Doped Silica Gradient-Index (GRIN) Lenses by Slurry-Based Three-Dimensional Printing (S-3DP™)

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ABSTRACT

The traditional Slurry-based Three-dimensional Printing (S-3DP™) process has been used to fabricate complex structure materials by printing organic binders in selected positions on each printing layer. This process is modified to fabricate functional graded materials, such as gradient index (GRIN) lenses, by depositing different concentrations of dopant at different positions. The modified S-3DP™ process offers advantages over conventional GRIN lens processes, including reduced processing time, improved compositional flexibility, and increased index profile dimensionality. Two different approximately parabolic dopant concentration profiles, which have maximum alumina concentrations of 1.63 mol% and 2.50 mol%, are printed into silica powder beds using S-3DP™. The samples with maximum alumina concentration of 1.63 mol% have been sintered into optical transparency at 1650 ^{0}C for 30 minutes in a vacuum furnace ($5x10^{-6}$ torr) while an additional dehydration process before sintering was required for the samples with maximum alumina concentration of 2.50 mol%. The magnifying effects of GRIN lenses with profiles of 1.63 mol% and 2.50 mol% alumina were observed, yielding effective focal lengths of 10 cm and 6.1 cm, respectively. Light diffraction, which results from the locally inhomogeneous dopant distribution and reduces the optical quality of GRIN lenses, was also observed.

INTRODUCTION

Conventional glass-based GRIN lenses have been fabricated by various methods, including molecular stuffing [1], ion exchange [2-7], and sol-gel [8,9] techniques, that rely on stuffing of base glass compositions with index altering cations. The diffusion-controlled nature of these processes requires long processing times (typically > 100 hours), thereby limiting feasible component sizes to less than 13 mm. In addition, GRIN materials fabricated by ion exchange techniques are not suitable for high temperature applications since the migration of alkali ions results in the distortion of the index profile [8]. Alternative materials systems or fabrication methods for large-scale GRIN components with desired optical characteristics and good environmental and thermal stability are needed.

The S-3DP™ technology is an agile, facile method of producing near-net shape advanced ceramic components. Parts are constructed in a layer-by-layer build sequence. Each layer of the

component is created by jetting a ceramic slurry onto a substrate, then selectively printing a binder into the dried layer in the desired pattern. The excess powder is then removed to produce a three dimensional structure. The S-3DP™ process can be modified to fabricate functionally graded materials, such as GRIN lenses, by replacing the binder with a dopant solution of varying concentration. The S-3DP™ process for GRIN lenses is shown schematically in Figure 1. Production of GRIN materials by S-3DP™ offers several advantages over conventional processing methods, including reduced processing times (< 70 hours) yielding economical fabrication of large-scale components, improved compositional flexibility, and increased index profile dimensionality. The improved flexibility and compositional control offered by S-3DP™ allows for a single component lens system with greater functionality. This reduces the number of optical components required, yielding considerable weight savings. The lens stacking required to overcome optical aberrations of a photographic lens system, for example, can be replaced by a single S-3DP™ GRIN lens.

This research focuses on developing an alumina-silica based materials system that can be used in the S-3DP™ process. The system was chosen because of the miscibility of alumina and silica at high temperature. The fabrication and properties of the resultant alumina-doped S-3DP™ GRIN lens are discussed in the following sections.

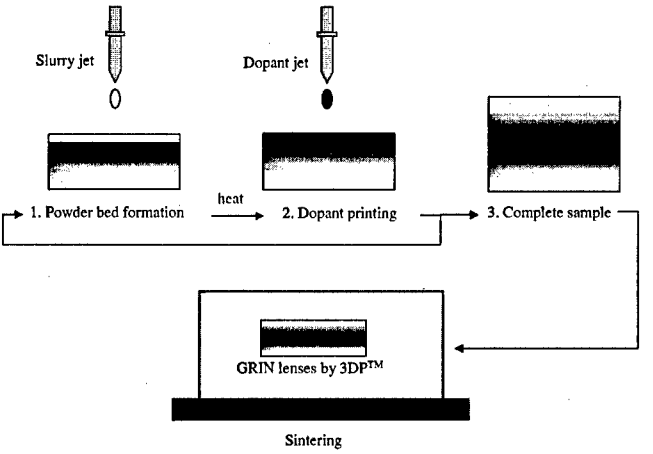


Figure 1. The schematic drawing of the S-3DP™ process for GRIN lenses.

EXPERIMENTAL PROCEDURE

The amorphous silica powder (Mitsubishi Chemical Company) used in this research had a median particle size of 1.4 μm and a surface area of 2.666 m^2/g. Aluminum nitrate nanohydrate ($Al(NO_3)_3*9H_2O$, Alfa Aesar) was used as the dopant source. The silica slurry with 30 vol% solid loading was prepared and ball-milled with glass media for 20 hours before printing. The chemical composition of the slurry is shown in Table I. Boric Acid was added to lower the sintering temperature. The alumina-doped powder beds were then made by S-3DP™. The

thickness of each printing layer was 73 μm. Two dopant concentration profiles, Design 2.5% max and Design 1.63% max, were deposited into the powder beds, as shown in Figure 2. The powder beds were heated to 900 °C for 4 hours to remove the hydroxyl groups introduced by the aluminum nitrate solution as well as the organic additives. Sintering was performed in a vacuum furnace (Centoor, MRF, pressure ~ $5x10^{-6}$ torr). Un-doped silica powder beds can be sintered to optical transparency at 1500 °C for 30 minutes. An additional dehydration process, 1000 °C for 24 hour in the vacuum furnace, was required for the powder beds with a maximum alumina concentration of 2.5 mol% before sintering. The alumina-doped powder beds were sintered at 1650 °C for 30 minutes. The sintered powder beds were polished and observed under an optical microscope. Electron Probe Micro Analysis (EPMA) was used to measure the dopant concentration profiles of the sintered samples.

Table I. The chemical composition of the silica slurry.

Silica Powder (vol%)	Deionized Water (vol%)	Methanol (vol%)	Poly(ethylene glycol) (MW:400)	NH_4OH (M)	H_3BO_3 (wt%)
30	35	35	3 wt% based on silica	0.20	1 wt% based on silica

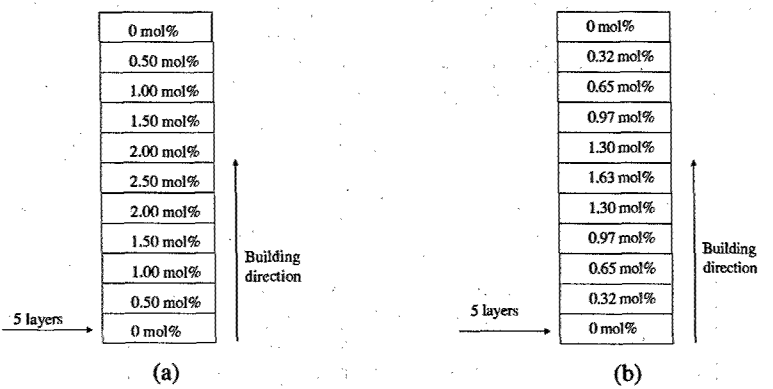


Figure 2. The concentration profiles of alumina in the GRIN lenses of (a) Design 2.5% max and (b) Design 1.63% max.

RESULTS AND DISCUSSION

The mixture of alumina and silica tends to form mullite ($3Al_2O_3+2SiO_2$) at temperatures higher than 950 °C [10]. The formation of mullite can be minimized by increasing the cooling rate and using an alumina concentration lower than 5 mol% [10]. The maximum alumina concentration in this study was 2.50 mol% (Figure 2). No crystallization in the alumina-doped

powder beds was found after heating at 900 °C for 4 hours. Several sintering conditions were tested. Optical transparency was achieved by sintering at 1650 °C for 30 minutes and cooling at the maximum rate (~500 °C per minute from the sintering temperature) allowed by the furnace. The magnifying effects of the sintered powder beds are shown in Figure 3. The MIT markers under the sintered GRIN lenses are enlarged in the vertical direction, as expected from the dopant concentration profiles shown in Figure 2. The object and image sizes in the vertical direction were measured, allowing the effective focal length (f_{eff}) to be determined by the following equation [11]:

$$\frac{1}{f_{\text{eff}}} = \frac{1}{S_1} - \frac{H_1}{H_2 * S_1} \tag{1}$$

where H_1 is the object size, H_2 is the image size, and S_1 is the distance between the lens and the object. The theoretical focal length (f_{th}) of a GRIN slab with a parabolic index of refraction profile is given by the following equation [12]:

$$f_{th} = \frac{1}{\left(\frac{n_{\max}^2 - n_{\min}^2}{0.25 w^2}\right)^{1/2} \sin\left(\frac{d}{0.5w}\left(1 - \frac{n_{\min}^2}{n_{\max}^2}\right)^{1/2}\right)} \tag{2}$$

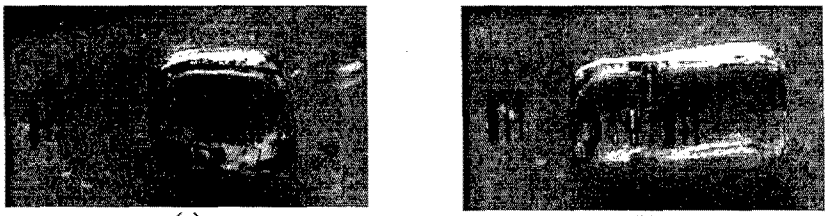
where w is the width of the GRIN slab, d is the thickness of the GRIN slab, n_{min} is the minimum index of refraction, and n_{max} is the maximum index of refraction. No direct measurement of index of refraction has been made. However, the index of refraction of the fused silicate (n) containing alumina has been studied and found to have a linear relationship with the alumina content [13] as:

$$n=1.4580+0.00192M \tag{3}$$

where M is the alumina concentration in mol%. The alumina concentration profiles of the Design 1.63% max and Design 2.5% max samples are shown in Figure 4. The profiles are fitted with parabolic curves. The maximum alumina concentrations of the Design 1.63% max and Design 2.5% max samples are found to be 1.04 mol% and 1.35 mol% and the maximum indexes of refraction (n_{max}) of both samples are calculated to be 1.46 and 1.4606 from Equation (3). The theoretical focal lengths of the sintered powder beds, assuming a parabolic index profile, are then calculated and compared with the effective focal lengths, as show in Table II. The effective focal length is very close to the theoretical values for the Design 1.63% max sample. The difference between the effective and theoretical values of the Design 2.5% max and Design 2.5% max(1) samples is due to the fact that the index profiles are not ideally parabolic. The actual concentrations are also lower than the designed values. This indicates that further research must be done to allow for more precise compositional control.

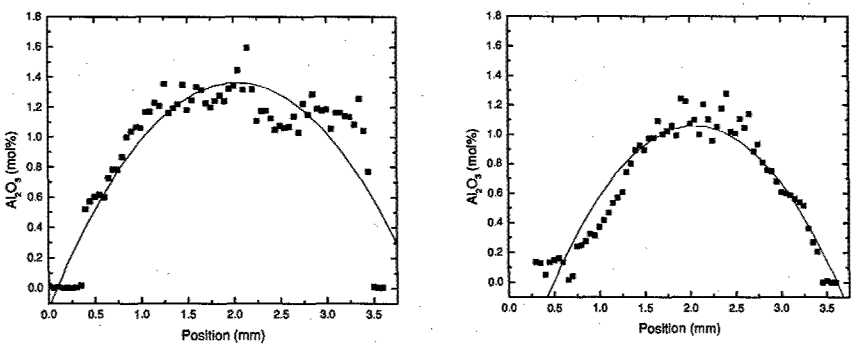
Observation of the sample perpendicular to the build direction shows a possibly problematic artifact of the printing process. The optical micrograph in Figure 5 and laser diffraction in Figure 6 show compositional variation within each layer. It is believed that the migration of dopant solution during the drying of each printed layer causes the non-uniform distribution of dopant within each layer. The locally high and low index regions within each layer diffract light

differently after the sample is sintered. Future research will focus on drying conditions and other methods to minimize this effect.



(a) (b)

Figure 3. The vertical enlargement with the GRIN lenses of (a) Design 2.5%(1) max and (b) Design 1.63% max above an MIT marker.



(a) (b)

Figure 4. The dopant distribution of the GRIN lenses of (a) Design 2.5% max(1) and (b) Design 1.63% max.

Table II. The effective (f_{eff}) and theoretical (f_{th}) focal lengths of different GRIN lenses.

	d (cm)	w (cm)	f_{eff}(cm)	f_{th} (cm)
Design 1.63% max	0.55	0.30	10	10.3
Design 2.5% max	0.70	0.30	4.68	6.27
Design 2.5% max (1)	0.60	0.30	6.10	7.28

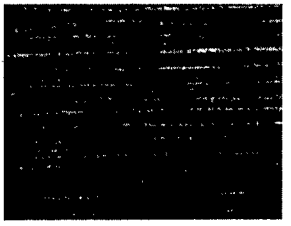


Figure 5. The layer merging problem investigated under the optical microscope.

Figure 6. The diffraction of the laser light shining through the sample.

CONCLUSIONS

The alumina-silica systems have been studied for the fabrication of GRIN lenses by S-3DP^{TM}. Optically transparent alumina-silica GRIN lenses were obtained by sintering at 1650 °C for 30 minutes. Three different GRIN lenses (Design 1.63% max, Design 2.5% max and Design 2.5% max(1)) with effective focal lengths of 10, 4.68, and 6.10 cm, respectively, have been successfully fabricated. EPMA results show the deviation of the actual dopant concentration from the designed value. Further research will focus on more precise local composition control and elimination of light diffraction due to locally inhomogeneous distribution of dopant.

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